

Corrosion Study of Pipeline Steel Weld Immersed in Sour Solution

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Abstract

This work presents an electrochemical study of API X52 pipeline steel weld immersed in NACE solution saturated with hydrogen sulphide (H₂S). The electrochemical techniques, polarization curves and linear polarization resistance are used in the corrosion test of the steel weld samples with the focus on the three different zones of the weldment, heat affected zone (HAZ), weld bead (WB) and base metal (BM). In addition, a brief analysis was made in order to identify the corrosion product film. It was found that the increment of temperature and H₂S dissolved in the NACE solution increase the corrosion rate (CR) of the three different zones. HAZ was significantly affected by the corrosion test and the phases mackinawite, troilite and pyrrhotite were identified in the film of corrosion products.

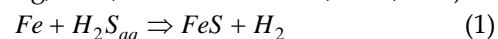
Keywords

Polarization Curves; LPR; X52 Pipeline Steel; H₂S

Introduction

For the majority of steels used in construction, most welding processes are acceptable from a corrosion point of view; provided that the welded joint had been made in a proper manner and the correct filler materials had been chosen (Wranglen, 1985). The failures of steel welded have been attributed to corrosion of the selective zones of the weld. This corrosion that found in fusion zone and electrical resistance welded, occurs in several environments, and is not confined to one region of the weldments (Loto, 1989). During the welding thermal cycle, a relatively narrow region of the material is subjected to a wide range of peak temperatures and cooling rates, resulting in a variety of microstructures and changes in properties of the affected area. Dominant mechanisms influencing the corrosion behaviour of the weld, should be attributed to the the formation of microstructures susceptible to corrosion and the redistribution of sulphides during the weld thermal cycle (Olsen, 1997). In addition to welding, the "sour environment" can produce failures in the structures and pipeline steel of the oil and chemical industries.

H₂S has been associated to damages by corrosion and stress corrosion cracking induced by sulphides or hydrogen (Cayard, 1997; Cheng, 1998; Huang, 1996). The increment of temperature and/or pressure can increase the aggressiveness of H₂S solution for the carbon steel. Steel corrosion in solutions containing H₂S can be represented according to following reactions (Ewing, 1955; Galván-Martínez, 2004,2005):



Most corrosion studies on API X52 steel in environments containing H₂S or sulphide ions put the emphasis on the use of the electrochemical techniques on the study of multiples factors that can affect the corrosion behaviour, such as H₂S concentrations (Perdomo, 2002), corrosion inhibitors (Vásquez, 2003; Romero, 2004), hydrodynamic conditions (Galván-Martínez, 2004,2005), microorganisms (Galvan-Martinez, 2005; Borgne, 2007) and mechanical stresses (Li, 2006; Lu,2006). Nevertheless, little work has addressed the corrosion study of the X52 steel weld in these environments. This work presents the electrochemical results obtained during the corrosion of the weldment of X52 pipeline steel sample focused on the three different weld zones.

Experimental Procedure

TABLE 1 NACE BRINE COMPOSITION

Chemical reagent	Weight (g/l)
calcium chloride dihydrate	4.48
magnesium chloride sixhydrate	2.06
sodium chloride	106.58

An aqueous NACE brine solution was used as test environment. Table 1 shows the reagents that constitute the composition of this brine. All the tests were carried out at two different temperatures, 25°C and 50°C, atmospheric pressure and static conditions. In order to remove oxygen from the test solution, N₂ gas was bubbled into the test solution for a period of 30 minutes, prior to the implementation of the test. After oxygen removal, H₂S gas was bubbled into the test

solution until saturation was reached. The measured saturation pH was 3.5. In Table 2, it is possible to observe the chemical composition of the API X52 steel.

TABLE 2. CHEMICAL COMPOSITION OF THE API X52 STEEL

C	Mn	Si	P	S	Cu	Cr
0.08	1.05	0.26	0.019	0.003	0.019	0.02
Ni	Nb	V	Ti	Al	Fe	
0.02	0.041	0.054	0.002	0.038	Balance	

Experimental Setup

The material studied was a longitudinal weld bead obtained from X52 pipeline steel. Three different zones were studied, HAZ, WB and BM. This weldment was produced by the submerged arc welding process. All electrochemical tests were carried out in a 1L air-tight electrochemical glass cell with a three electrodes array. Working electrode (WE) was made according to different zones of the longitudinal weld bead. The WE used had the following total exposed areas: 1 cm² for WB specimens, 0.1 cm² for HAZ specimens and 1 cm² to BM specimens. Before each test, the WE was polished with silicon carbide (SiC) paper up to 600 grit, and then it was cleaned with deionised water, degreased with acetone and kept in a desiccator. The reference electrode used was a saturated calomel electrode (SCE) and a sintered graphite rod was used as auxiliary electrode (AE).

Electrochemical Measurements

The electrochemical measurements referred to SCE were:

- Corrosion potential (E_{corr}) against time.
- Linear Polarization Resistance (LPR). The potential range used was ± 0.015 V referred to E_{corr} and a sweep rate of 0.001 Vs⁻¹. In all calculations of the corrosion rate, the experimental value of the Stern-Geary constant was considered.
- Polarization curves (PCs) were recorded at a sweep rate of 0.001 Vs⁻¹, the potential range used was ± 0.5 V referred to E_{corr} .

Electrochemical measurements were carried out at several time intervals during the exposure time. After exposure, selected samples were used in order to analyse the chemical composition of the corrosion products by Energy Dispersive X-Ray (EDX) emission analysis through a Scanning Electron Microscope (SEM) and X-Ray Diffraction (XRD).

Results and Discussion

Corrosion Potential, E_{corr} .

Fig. 1 shows the variation of the measured E_{corr} with

the time exposition in the test solution without and with H₂S. In both conditions (NACE brine with and without H₂S), it is possible to observe that, the measured values of the E_{corr} corresponding to HAZ are more electronegative than E_{corr} values of the WB and BM.

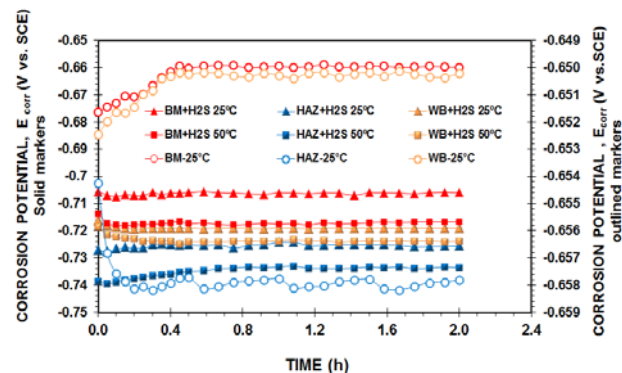


FIG. 1 E_{corr} AS A FUNCTION OF TIME OF THE X52 STEEL IN TEST SOLUTION WITHOUT AND WITH H₂S AT 25°C AND 50°C

The E_{corr} values of the WB also are more electronegative than E_{corr} values of the BM. In addition, it is important to note that at 25°C, all values of the E_{corr} corresponding to NACE brine with H₂S are more electronegative than the E_{corr} values of the NACE brine without H₂S. This behaviour shows that the E_{corr} of the three weld zones of the carbon steel have been affected by the H₂S dissolved in the test environment.

Corrosion Rate, CR (LPR test)

Fig. 2 shows the variation with the time of the experimental CR values obtained in the LPR tests. It is clear that temperature affects the measured CR. In NACE brine with H₂S, CR rises as the temperature increases.

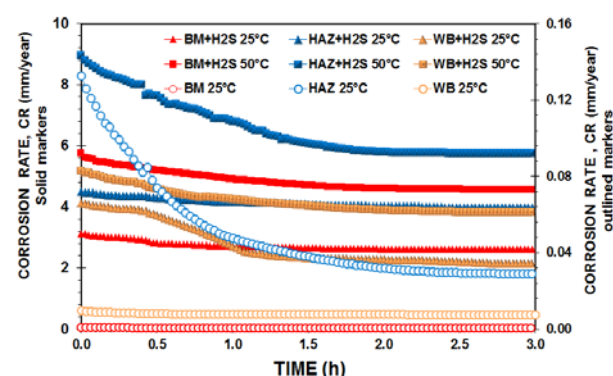


FIG. 2 CR CALCULATED BY LPR AS A FUNCTION OF TIME. X52 STEEL WELD IN TEST SOLUTION WITHOUT AND WITH H₂S AT 25°C AND 50°C.

This temperature effects is important because the transfer of electrochemical species from the bulk to surface of the X52 pipeline steel weld, FeS formation, and the charge transfer in the corrosion process (Arzola-Peralta, 2006) is promoted. At 25°C, the

highest CR was measured in the NACE brine with H₂S; and this behaviour could be attributed to the fact that H₂S gas can be dissolved in aqueous environment in which it can be turned into corrosive solutions (Galván-Martínez, 2004,2005; Seki, 1982).

It is important to point out that, in both brines (with and without H₂S), the highest CR was measured in the HAZ of the weldment and the CR of the WB zone is higher than BM zone. This behaviour could be attributed to the variation in the microstructure (grain size) and residual stresses (Sephton, 2000).

In addition, at the beginning of the test, all measured CR moves to higher values and as the exposure time increases, the CR changes to stable values. This behaviour can be due to the fact that at the beginning of the test, the surface of the steel was clean and consequently active. After a period of time, a corrosion product film was formed on the working electrode surface insulating partially the metal surface from the test solution, and reduced with this fact the corrosion rate. According to some researchers, the first product of the film formed in the corrosion of the steel in sour environment is mainly mackinawite (R. Galvan – Martinez, 2005; Videm, 1995; Vedage, 1993).

Polarization Curves (PCs)

Fig. 3 shows the PCs of the steel in NACE brine without and with H₂S at 25°C and 50°C. Table 3 presents the corrosion parameters calculated from the PCs. Fig. 3 shows that all corrosion current densities (i_{corr}) in NACE brine with H₂S at 50°C are higher than i_{corr} in NACE brine with and without H₂S at 25°C; consequently the calculated CR values have the same behaviour. It is important to point out that the cathodic branches in the PCs shown in figure 3a have slopes (0.18 V/decade approximately) that can not be associated to a pure charge transfer (Galvan – Martinez, 2005). This feature suggests a contribution of a mass transfer process (mainly H⁺) to the cathodic kinetics.

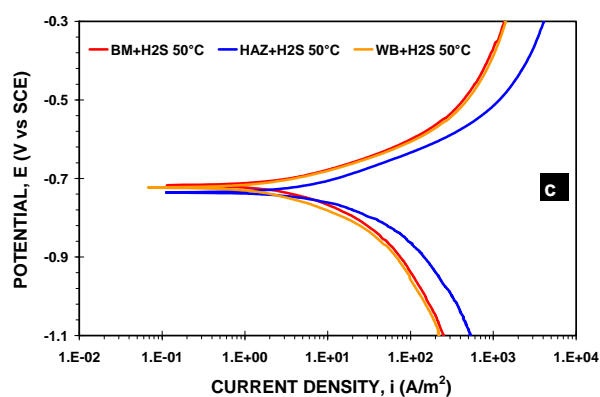
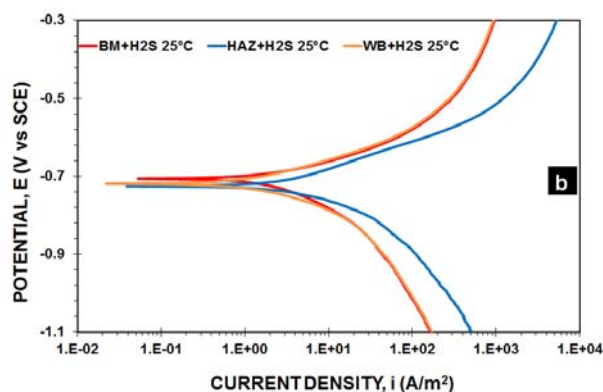
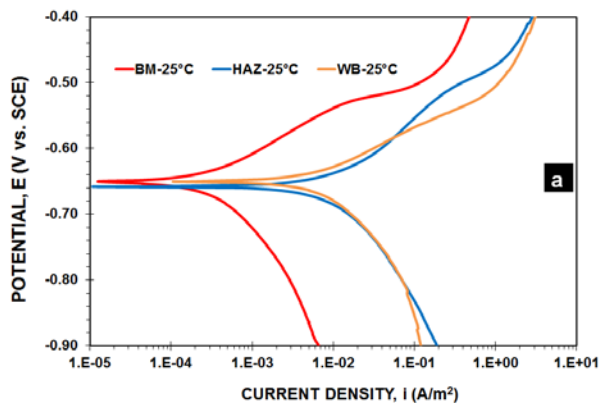


FIG. 3 PCs OF THE X52 STEEL WELD IN TEST SOLUTION WITHOUT (a) AND WITH H₂S AT 25°C (b) AND 50°C (c).

On the other hand, the PCs shown in figure 3b and 3c have cathodic branches that could be related with a charge transfer process. The corrosion parameter obtained by the polarization curves, and the corrosion rate calculated from these parameters can be observed in table 3. According to table 3, the CR values obtained by polarization curves has the same behaviour that the CR values obtained by LPR test; the CR increases as the temperature also rises and at 25°C, the CR values in NACE brine with H₂S are higher than those in NACE without H₂S. Finally, it is important to point out that the calculated CR values in HAZ are higher than those obtained in the BM and WB.

TABLE 3 CORROSION PARAMETERS OBTAINED FROM THE PCs SHOWN IN FIG. 3

Test Solution	Weld Zone	B _{Exp.} (V)	i_{corr} (A / m ²)	CR (mm/year)
NACE without H ₂ S at 25°C	BM	0.022	3.20E-04	0.00037
	HAZ	0.026	1.00E-02	0.01159
	WB	0.021	6.35E-03	0.00736
NACE with H ₂ S at 25°C.	BM	0.020	2.30E+00	2.66678
	HAZ	0.019	3.40E+00	3.94219
	WB	0.018	1.65E+00	1.91312
NACE with H ₂ S at 50°C.	BM	0.022	4.20E+00	4.86977
	HAZ	0.017	5.20E+00	6.02923
	WB	0.019	3.00E+00	3.47840

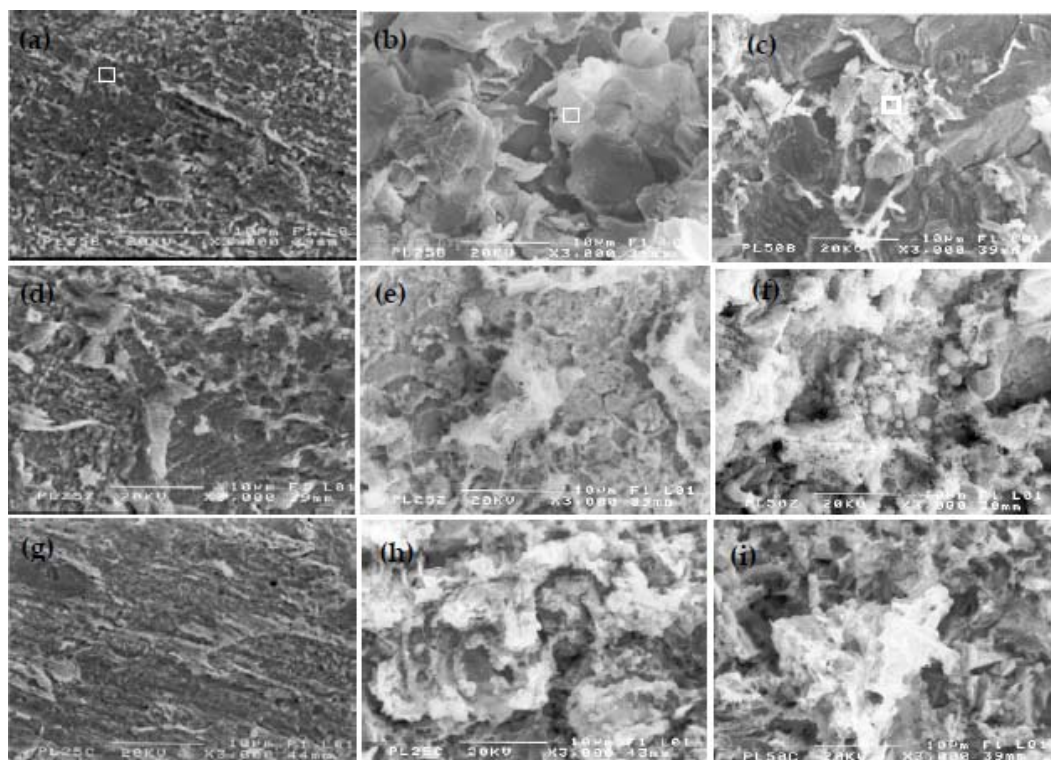


FIG. 4 SEM MICROGRAPHS OF THE CORROSION PRODUCTS FILM OBTAINED FROM THE WELDMENT EXPOSED TO THE NACE BRINE WITHOUT H₂S (a, d, g) AND NACE BRINE WITH H₂S AT 25°C (b, e, h) AND 50°C (c, f, i).

Surface Analysis

Fig. 4 shows a micrograph obtained by SEM from the three different zones of the weldment (Fig. 4a to 4c BM, Fig. 4d to 4f HAZ and Fig. 4g to 4i WB) exposed to the NACE brine solution without and with H₂S. These micrographs show the corrosion product film formed on steel surface at 25°C and 50°C and both condition (with and without H₂S). The squares shown in each micrograph indicate the analyzed area by SEM.

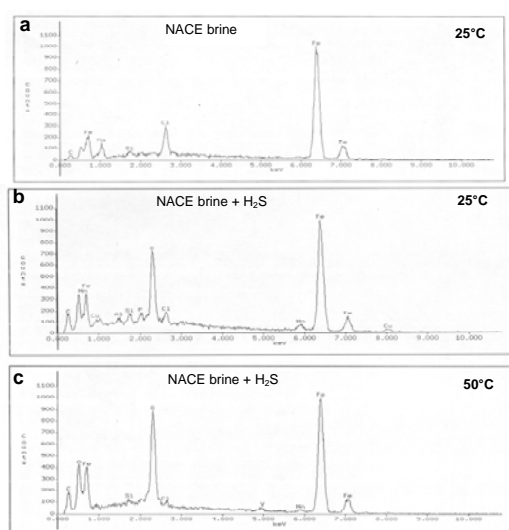


FIG. 5. CHEMICAL MICROANALYSIS OF THE BM EXPOSED TO NACE BRINE SOLUTION WITHOUT (5A) AND WITH H₂S AT 25°C (5B) AND 50°C (5C).

Fig. 5 shows a chemical microanalysis corresponding

to the sample tested in NACE brine without H₂S (5a) and with H₂S at 25°C (5b) and 50°C (5c).

The chemical microanalysis was obtained from the sample of the BM. In Fig. 5a, the EDX spectrum shows that the two elements with major concentration in the corrosion products film are chloride (Cl) and iron (Fe). These elements constitute the iron chloride film formed in seawater environment (Mercer, 1990). According to XRD results obtained in samples tested at 25°C, lawrencite (FeCl₂) and molysite (FeCl₃) were the main corrosion products found.

In figures 5b and 5c, the EDX spectra show that the two elements with major concentration in the corrosion products film are sulphur (S) and iron (Fe). These elements constitute the iron sulphur film formed in H₂S environments. According to XRD results, mackinawite (Fe_{1-x}S) was the corrosion product found at 25°C. It is important to point out that, when the temperature increases at 50°C, mackinawite, Troilite (FeS) and Pyrrhotite (Fe_{1-x}S) were found. These results are agreed with the results obtained by some researchers (Shoesmith, 1980; Tewary, 1979; Wikjord, 1980; Pound, 1989) about the steel corrosion in aqueous solution containing dissolved H₂S.

Conclusions

The electrochemical measurements at 25°C show that

the CR calculated from the welding of the X52 steel in NACE brine with H₂S is higher than that calculated in NACE brine without H₂S. This fact can be attributed to the H₂S because it turns the NACE brine solution more corrosive. In general, in NACE brine with and without H₂S, the CR in HAZ is higher than that in the WB and as well the corrosion rate in WB is higher than that in the BM. This behaviour could be attributed to the variation in microstructure (grain size) and residual stresses. The CR in NACE brine with H₂S increases as the temperature also increases from 25°C to 50°C. This temperature effects promote the transfer of electrochemical species from the bulk to the surface of the welding of X52 pipeline steel and the charge transfer in the corrosion process. In NACE brine with and without H₂S at 25°C and 50°C, the calculated CR decreases with the increment of exposure time. This behaviour can be attributed to the formation of a corrosion products film on surface of the X52 pipeline steel weld. According to surface analysis, the corrosion product film that covered the surface of the X52 pipeline steel weld in NACE brine without H₂S at 25°C was iron chloride, whereas the sample in NACE brine with H₂S at 25°C and 50°C was iron sulphide. In addition, the iron sulphide formed on surface of the X52 pipeline steel weld at 25°C was mackinawite, and when the temperature increases from 25°C to 50°C, mackinawite, troilite and pyrrhotite were found.

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